

# The Curie temperature and exchange energy between two sublattices in half-metallic greigite $\text{Fe}_3\text{S}_4$

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High-temperature magnetic measurements have been carried out in hydrothermally synthesized greigite ( $\text{Fe}_3\text{S}_4$ ). We show that the Curie temperature of greigite is significantly lower than that for its iron oxide counterpart  $\text{Fe}_3\text{O}_4$ . The lower  $T_C$  value (about 677 K) of greigite is in quantitative agreement with that calculated using the exchange energy (3.25 meV) and the spin values of the two sublattices, which are inferred from the neutron and magnetization data of high-quality pure greigite samples. We further show that, with an effective on-site Hubbard energy  $U_{eff} = 1.16$  eV, the lattice constant and two sublattice spins predicted from *ab initio* density-function theory are in nearly perfect agreement with the measured values. The parameter  $U_{eff} = 1.16$  eV ensures  $\text{Fe}_3\text{S}_4$  to be an excellent half-metallic material for spintronic applications.

Greigite ( $\text{Fe}_3\text{S}_4$ ) that was first discovered in lake sediments from California [1] is an iron thiospinel. Greigite was found to have the inverse spinel structure [1] like its iron oxide counterpart, magnetite ( $\text{Fe}_3\text{O}_4$ ). Greigite has been used as a recorder of the ancient geomagnetic field and environmental processes and is important for paleomagnetic and environmental magnetic studies [2–4]. It is also widespread in magnetotactic bacteria that produce greigite magnetosomes [5–7]. Therefore, greigite is of general interest in geophysics and biology.

On the other hand, greigite has been less known to physicists and material scientists because pure greigite samples are difficult to synthesize and some of its fundamental magnetic properties are still unknown. The precise value of the Curie temperature  $T_C$  remains unknown despite variable estimations since 1974. The difficulty in determination of the Curie temperature is due to the fact that greigite is chemically unstable at high temperatures even in argon environment [8]. High-temperature magnetic measurements often revealed chemical decomposition that precluded from determination of the Curie temperature [8, 9]. Spender *et al.* [10] estimated  $T_C$  to be 606 K by extrapolating thermomagnetic curves to high temperatures. Vandenbergh *et al.* [11] made Mössbauer spectroscopic measurements up to 480 K and extrapolated the effective field of iron in tetrahedral sites to obtain a  $T_C$  value of at least 800 K. More recent magnetic measurements on high-quality pure greigite samples [12] suggested a Curie temperature of higher than 630 K. Therefore, the reported Curie temperature of greigite ranges from 600 K to 800 K.

Another important magnetic property is the saturation magnetization which is associated with the spin values of  $(\text{Fe}^{3+})_A$  and  $(\text{Fe}^{3+}\text{Fe}^{2+})_B$  on the respective tetrahedral (A) and octahedral (B) sublattices. Coey *et al.* [13] suggested that greigite should have a net magnetic moment  $m > 4 \mu_B$  per formula unit considering the spin-only values for the ionic moments. They could not account for the measured magnetic moment of  $2.2 \mu_B$ . Recent neutron diffraction experiments on high-quality pure greigite

samples [14] indicate a much larger net magnetic moment of  $3.4 \mu_B$ . Devey *et al.* [15] studied the electronic and magnetic behaviors of this material using *ab initio* density-functional theory in the generalized gradient approximation (GGA) with the on-site Hubbard energy  $U_{eff}$  parameter (GGA + U). They calculated the lattice constant  $a$  and two sublattice moments ( $m_A$  and  $m_B$ ) as a function of  $U_{eff}$ . Comparing the measured lattice constant with their calculated results [15], they found that  $U_{eff} \simeq 1$  eV. This  $U_{eff}$  value leads to  $m_A \simeq m_B \simeq 3 \mu_B$ , in quantitative agreement the measured values from neutron diffraction [14].

Here we report high-temperature magnetic measurements on hydrothermally synthesized greigite. We show that the Curie temperature of greigite is significantly lower than that for its iron oxide counterpart  $\text{Fe}_3\text{O}_4$ . The lower  $T_C$  value (about 677 K) of greigite is in quantitative agreement with that calculated using the exchange energy (3.25 meV) and the spin values of the two sublattices, which are inferred from the neutron [14] and magnetization [12] data of high-quality pure greigite samples. We further show that, with an effective on-site Hubbard energy  $U_{eff} = 1.16$  eV, the lattice constant and two sublattice spins predicted from *ab initio* density-function theory [15] are in quantitative agreement with the measured values. The parameter  $U_{eff} = 1.16$  eV ensures  $\text{Fe}_3\text{S}_4$  to be an excellent half-metallic material for spintronic applications.

Greigite samples were synthesized under a magnetic field with a hydrothermal route [16]. Briefly, ammonium iron sulfate hexahydrate (0.2 mmol) and cysteine (1 mmol) were dissolved in distilled water (25 mL) and stirred vigorously for 50 min. The solution was then put into a 30 mL Teflon vessel with two circular magnets (2.5 kOe) at the top and bottom in a stainless steel autoclave. After 12 h reaction at 180 °C, black products were obtained. These products were washed several times in distilled water and pure ethanol to remove impurities. These samples were dried in vacuum at 60 °C for at least 6 h.

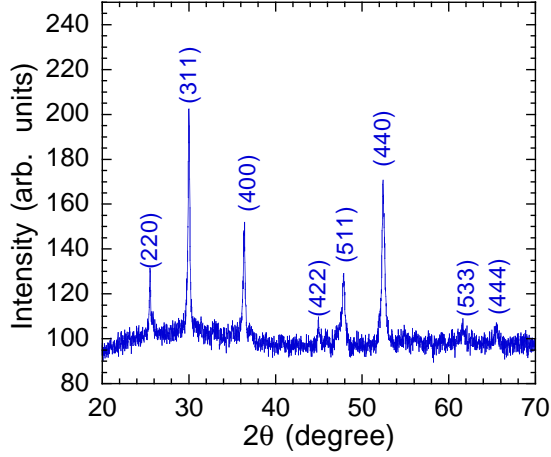


FIG. 1: X-ray diffraction (XRD) spectrum for a greigite sample synthesized under a magnetic field of 2.5 kOe. All the peaks can be indexed by the spinel  $\text{Fe}_3\text{S}_4$  phase with a lattice constant  $a = 9.877 \text{ \AA}$ . The mean diameter of the crystallites (subparticles) is determined to be about 36 nm from the width of the (311) peak.

Samples were checked by x-ray diffraction (XRD) right after synthesis. Fig. 1a shows XRD spectrum for a greigite sample synthesized under a magnetic field of 2.5 kOe. All the peaks can be indexed by the spinel  $\text{Fe}_3\text{S}_4$  phase. The lattice constant  $a$  is evaluated to be  $9.877 \text{ \AA}$ , in excellent agreement with the reported value ( $9.876 \text{ \AA}$ ) [1, 14]. The mean diameter of the crystallites (subparticles) is determined to be about 36 nm from the width of the (311) peak.

Magnetization was measured using a Quantum Design vibrating sample magnetometer (VSM). The moment measurement was carried out after the sample chamber reached a high vacuum of better than  $9 \times 10^{-6}$  torr. The absolute measurement uncertainties in temperature and moment are less than 10 K and  $1 \times 10^{-6}$  emu, respectively. We used the same heating and cooling rate of 30 K/min for thermomagnetic measurements, which can ensure a thermal lag of less than 10 K.

In Fig. 2, we plot magnetic hysteresis loop at 300 K for the greigite sample. Since the magnetization is almost saturated at a magnetic field of 20 kOe, we can take the magnetization at 20 kOe to be the saturation magnetization  $M_s$ . The  $M_s$  value is found to be about 40 emu/g, which is close to that of the similarly prepared sample [16] but significantly below the value (59 emu/g) reported for high-quality greigite samples with  $d = 14 \mu\text{m}$  (Ref. [12]). The reduction of the  $M_s$  value in our sample may be due to both finite-size effects [17] and possible presence of nonmagnetic amorphous phases.

Figure 3a shows the temperature dependence of the magnetization for the greigite sample, which was measured in a magnetic field of 10 kOe. The warm-up data up to 780 K indicate a magnetic transition around 700 K. A substantial magnetization between 720 and 780 K implies that a small fraction of the  $\text{Fe}_3\text{S}_4$  phase was con-

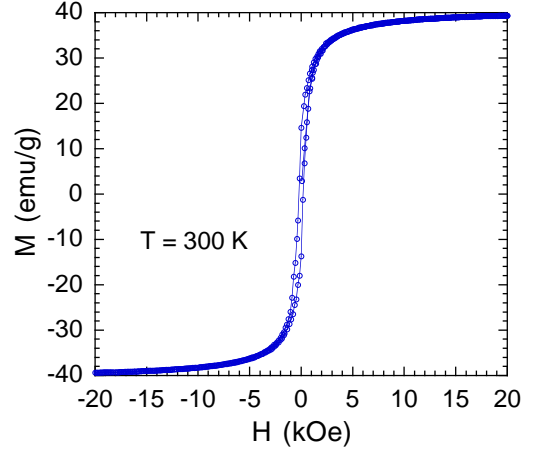


FIG. 2: Magnetization versus magnetic field at 300 K. The saturation magnetization  $M_s$  is found to be about 40 emu/g.

verted to the magnetic  $\text{Fe}_3\text{O}_4$  phase in this temperature regime. Since this sample was measured after the VSM high-vacuum cryopump was exposed to air during a service and regenerated through evacuation by a mechanic pump, it is likely that there is a minor oxygen contamination that may promote a chemical alteration to the  $\text{Fe}_3\text{O}_4$  phase below 700 K.

After the sample was cooled down from 780 K with a rate of 30 K/min, the magnetic transition around 700 K disappeared and the magnetization at room temperature was reduced to about 30% of the initial value, indicating that the  $\text{Fe}_3\text{S}_4$  phase was completely decomposed into other phases (e.g.,  $\text{Fe}_3\text{O}_4$  and nonmagnetic ferrosulfides such as  $\text{FeS}_2$  [8]) after the high-temperature magnetic measurement.

In order to see the magnetic transition more clearly, we plot the derivative ( $dM/dT$ ) of the warm-up magnetization with respect to temperature. It is apparent that a minimum in  $dM/dT$  occurs at a temperature of about 677 K. The temperature corresponding to the minimum in  $dM/dT$  or the inflection point of the  $M(T)$  curve should be the Curie temperature of greigite, that is,  $T_C \simeq 677 \text{ K}$ . There is also a second local minimum at about 599 K, which happens to the same as the Curie temperature of  $\text{Fe}_7\text{S}_8$  (Ref. [18]). This suggests that a small fraction of the  $\text{Fe}_3\text{S}_4$  phase was converted to the  $\text{Fe}_7\text{S}_8$  phase even at a temperature below 599 K. Since the oxygen contamination in our VSM system is so minor and the warming rate is high (30 K/min), the remaining  $\text{Fe}_3\text{S}_4$  phase is still substantial when the Curie temperature of the phase is reached. This allows us to determine the Curie temperature of  $\text{Fe}_3\text{S}_4$  quite reliably. The magnetic transition at 677 K should be associated with the ferrimagnetic transition of greigite unless  $\text{Fe}_3\text{S}_4$  would have been converted to an unknown magnetic iron sulfide phase.

Our data suggest that the intrinsic Curie temperature of greigite is about 677 K. The intrinsic net moment of greigite has been determined to be about  $3.4 \mu_B$  per formula unit from both magnetization [12] and neutron

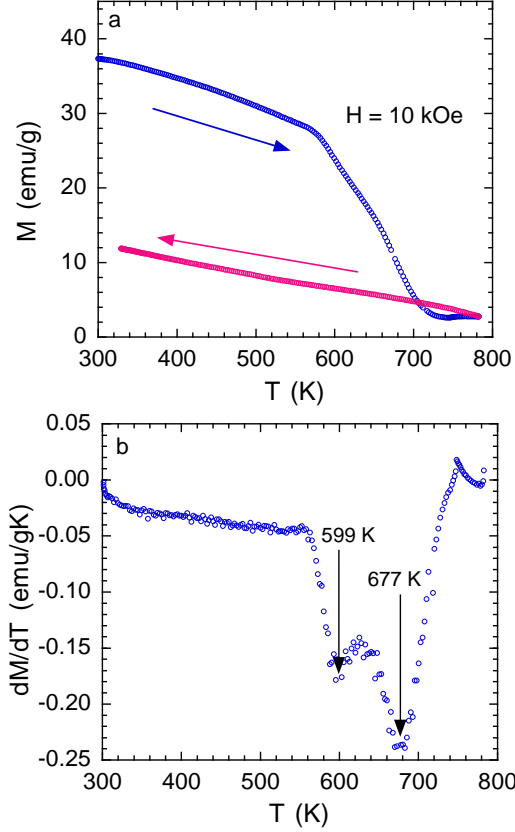


FIG. 3: a) Temperature dependence of the magnetization for sample A, which was measured in a field of 10 kOe. b) Temperature dependence of the derivative of the warm-up magnetization.

[14] data. Both the Curie temperature and the magnetic moment of greigite are significantly lower than those of its counterpart  $\text{Fe}_3\text{O}_4$ .

In order to quantitatively understand the differences between the two spinels, we need to consistently extract the exchange energy  $J_{AB}$  between the A and B sublattices for these two compounds. One way to determine  $J_{AB}$  is from the temperature dependence of the saturation (or high-field) magnetization at low temperatures. Since exchange energies ( $J_{AA}$  and  $J_{BB}$ ) between ions in the same sublattice of the inverse spinel structure are negligibly small [19], we can neglect these exchange energies and only keep  $J_{AB}$ . Within this approximation, the dispersion relation for the acoustic magnon to order  $k^2$  is [19]:

$$\hbar\omega = \frac{22}{16} \frac{J_{AB}S_AS_B}{2S_B - S_A} k^2 a^2, \quad (1)$$

where  $\omega$  is the frequency and  $k$  is the wave-number of the spin wave. From this dispersion, one can readily obtain a relation for the saturation magnetization at low

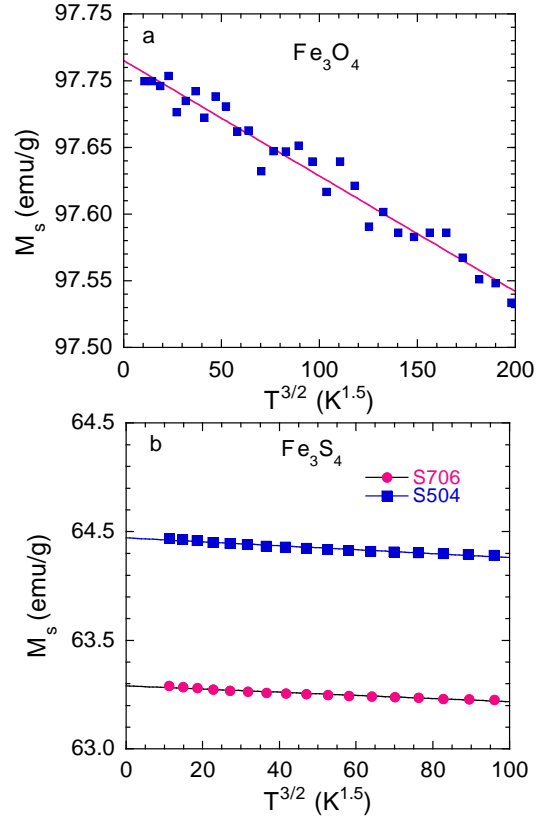


FIG. 4: a) Low-temperature saturation magnetization versus  $T^{3/2}$  for a  $\text{Fe}_3\text{O}_4$  crystal. The data are extracted from Ref. [20]. b) Low-temperature saturation magnetizations versus  $T^{3/2}$  for two  $\text{Fe}_3\text{S}_4$  samples (S706 and S504). The data are taken from Ref. [12].

temperatures:  $M_s(T) = M_s(0)(1 - CT^{3/2})$  with [20]

$$C = \frac{0.05864}{4(2S_B - S_A)} \left[ \frac{16(2S_B - S_A)k_B}{22J_{AB}S_AS_B} \right]^{3/2}, \quad (2)$$

where  $k_B$  is the Boltzman's constant.

In Figure 4, we plot low-temperature saturation magnetizations versus  $T^{3/2}$  for a  $\text{Fe}_3\text{O}_4$  crystal (Fig. 4a) and for two  $\text{Fe}_3\text{S}_4$  samples (Fig. 4b). The data for the  $\text{Fe}_3\text{O}_4$  crystal are extracted from Ref. [20] and the data for two  $\text{Fe}_3\text{S}_4$  samples are from Ref. [12]. The best linear fits to the data yield  $C = (8.9 \pm 0.3) \times 10^{-6} \text{ K}^{-1.5}$  for  $\text{Fe}_3\text{O}_4$ ;  $C = (1.15 \pm 0.06) \times 10^{-5} \text{ K}^{-1.5}$  for sample S706;  $C = (1.42 \pm 0.07) \times 10^{-5} \text{ K}^{-1.5}$  for sample S504. The average  $C$  value for  $\text{Fe}_3\text{S}_4$  is calculated to be  $1.29 \times 10^{-5} \text{ K}^{-1.5}$ .

For  $\text{Fe}_3\text{O}_4$ ,  $S_A = 2.5$  and  $S_B = 2.25$  (Ref. [19]). Substituting  $C = (8.9 \pm 0.3) \times 10^{-6} \text{ K}^{-1.5}$ ,  $S_A = 2.5$ , and  $S_B = 2.25$  into Eq. (2) yields  $J_{AB}/k_B = 22.7 \pm 0.6 \text{ K}$ , which is slightly below the value (27.8 K) determined directly from neutron scattering [19]. For  $\text{Fe}_3\text{S}_4$ , the two sublattice moments have also been determined by neutron

diffraction [14]. From the measured values [14]:  $m_A = 3.08 \mu_B$  and  $m_B = 3.25 \mu_B$ , we find  $S_A = 1.54$  and  $S_B = 1.63$ . Substituting  $S_A = 1.54$ ,  $S_B = 1.63$ , and the average  $C$  value of  $1.29 \times 10^{-5} \text{ K}^{-1.5}$  into Eq. (2), we find  $J_{AB}/k_B = 37.7 \text{ K}$ .

With neglect of exchange interactions between ions in the same sublattice of the inverse spinel structure, the Curie temperature within a mean-field approximation is given by [21]:

$$T_C^{MF} = 4\sqrt{2}(J_{AB}/k_B)\sqrt{S_AS_B(S_A+1)(S_B+1)} \quad (3)$$

Since the mean-field theory tends to overestimate the Curie temperature. Corrections to the mean-field theory were given for different structures such as simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc) [22]. Since the magnetic structure for the inverse spinel is fcc [19], the theoretical Curie temperature  $T_C$  after the correction to the mean-field theory is [22]:

$$T_C = 0.789[1 - 0.13/\sqrt{S_AS_B(S_A+1)(S_B+1)}]T_C^{MF}. \quad (4)$$

For  $\text{Fe}_3\text{O}_4$ ,  $S_A = 2.5$ ,  $S_B = 2.25$ , and  $J_{AB}/k_B = 22.7 \pm 0.6 \text{ K}$ . Substituting these numbers into Eqs. (3) and (4), we find that  $T_C = 808 \pm 22 \text{ K}$ , which is slightly below the measured  $T_C = 851 \text{ K}$  for  $\text{Fe}_3\text{O}_4$  (Ref. [20]). For  $\text{Fe}_3\text{S}_4$ ,  $S_A = 1.54$ ,  $S_B = 1.63$ , and  $J_{AB}/k_B = 37.7 \text{ K}$ . Plugging these values into Eqs. (3) and (4) yields  $T_C = 667 \text{ K}$ , slightly below the measured value of  $677 \text{ K}$ . This quantitative agreement suggests that the sublattice moments obtained from the neutron diffraction [14] and the Curie temperature measured in this work represent the intrinsic magnetic properties of greigite.

Now we compare the first principle calculations [15] with the experimental results. Comparing the measured lattice constant  $a = 9.8538 \text{ \AA}$  at  $10 \text{ K}$  (Ref. [14]) with the calculated results [15] yields  $U_{eff} = 1.16 \text{ eV}$ ,  $m_A = 3.05 \mu_B$ , and  $m_B = 3.26 \mu_B$ . The predicted sublattice moments are in quantitative agreement with the measured values [14]:  $m_A = 3.08 \pm 0.08 \mu_B$  and  $m_B = 3.25 \pm 0.08 \mu_B$ . This quantitative agreement implies that the first principle calculations based on the GGA + U model is very reliable. This also implies that the inferred parameter  $U_{eff} = 1.16 \text{ eV}$  is intrinsic to  $\text{Fe}_3\text{S}_4$ . This parameter  $U_{eff} = 1.16 \text{ eV}$  is very important since it ensures greigite to be a half metal [15]. Compared with other half metals such as  $\text{CrO}_2$  (Ref. [23]) and doped manganites [24–26], greigite should be better for spintronic applications because it has a much higher Curie temperature than those of  $\text{CrO}_2$  and doped manganites. Compared with the half-metallic magnetite (Ref. [27]),  $\text{Fe}_3\text{S}_4$  is also better for spintronic applications because it exhibits a highly conductive metallic behavior [28] in contrast to semiconductor-like electrical transport in  $\text{Fe}_3\text{O}_4$  [29]. Therefore, greigite is an excellent half-metallic material for spintronic applications.

In summary, we have determined the intrinsic Curie temperature ( $677 \text{ K}$ ) and exchange energy ( $3.25 \text{ meV}$ ) between the two sublattices of greigite. The measured Curie temperature is in quantitative agreement with that calculated using the exchange energy and the spin values of the two sublattices, which are independently determined from the neutron and magnetization data of high-quality pure greigite samples [12, 14]. We further show that, with an effective on-site Hubbard energy  $U_{eff} = 1.16 \text{ eV}$ , the lattice constant and two sublattice spins predicted from *ab initio* density-function theory are in nearly perfect agreement with the measured values. The parameter  $U_{eff} = 1.16 \text{ eV}$  ensures  $\text{Fe}_3\text{S}_4$  to be an excellent half-metallic material for spintronic applications. The current work will benefit to scientists working in multiple disciplines including physics, materials science and technology, geophysics, geochemistry, and biology.

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